

Observation-Based Quantification of Seasonal to Interannual Changes in Air-Sea CO₂ Fluxes

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1. INTRODUCTION

The ocean is the primary long-term sink for anthropogenic CO₂ taking up, on average, 1.5-2 Pg C yr⁻¹, or about 20-30% of the current annual release of anthropogenic CO₂. However, the oceanic uptake of CO₂ is highly variable in time and space. To be able to provide meaningful predictions of future atmospheric CO₂ levels, including the possible feedbacks on oceanic partial pressure of CO₂ (pCO_{2sw}), in response to climate and global change a high priority is placed on determining pCO_{2sw} fields and the derived air-sea CO₂ fluxes as part of the interagency US Ocean Carbon and Biogeochemistry Program (OCB). This effort provides and interprets CO₂ flux maps using a combination of *in situ* observations of pCO₂ from Volunteer Observing Ships (VOS), pCO₂ climatological data, and remotely sensed and assimilated sea surface temperature (SST) and wind products (NCEP II). High resolution *in situ* mixed layer depths are being tried as a predictor of pCO_{2sw}. The work is based on the basic premise is that the spatial distributions of pCO_{2sw} at seasonal resolution can be established through simple regional correlations of pCO_{2sw} with SST and other parameters that directly or indirectly control the pCO_{2sw} dynamics in surface water. This is a powerful approach to address the problem of interannual variability of pCO_{2sw} that is inherently data limited. The focus is on developing and validating methods to determine seasonal to interannual variability in the air-sea CO₂ flux over the past two decades.

2. PROJECT GOALS

We are applying innovative methods to estimate seasonal to interannual air-sea CO₂ fluxes utilizing the updated air sea CO₂ climatology of Takahashi et al. (2009), the large observational database of surface pCO₂ measurements from ships of opportunities and moorings from the SOCAT database (see, <http://ioc3.unesco.org/ioccp/Synthesis.html>), and winds to produce high-resolution estimates of the fluxes. The focus is on quantifying flux anomalies on seasonal to interannual timescale through determining regional algorithms of partial pressure of CO₂ in seawater, pCO_{2sw}, with remotely sensed and assimilated parameters. The effort involves a basic research component of understanding the causes of the variability and its relationship to climate indices such as ENSO, and product delivery of seasonal fluxes. The product that is developed is an automated routine to estimate seasonal air-sea CO₂ fluxes within 6 to 12-months of present utilizing remotely sensed SST from NCEP, the "Reynolds" optimal interpolated SST (Reynolds et al. 2007), and NCEP II re-analysis winds. In addition, there is ongoing research on improving the estimates and to improve the mechanistic understanding of the controls on pCO_{2sw}. These research efforts are done in a systematic fashion that include using updated pCO_{2sw} values, investigating the fidelity of the pCO₂/SST relationships by region, utilizing improved remotely sensed, assimilation and in situ products, and investigating the utility of other products such as

salinity and mixed layer depth obtained from the FOAM assimilation model. The scope of the research has expanded from what was proposed in that this effort is providing partial support to serving a regional ocean acidification product (Gledhill et al., 2008). Furthermore, there is stronger collaboration with modeling groups and international efforts than originally proposed.

The specific components of the effort as outlined in the proposal and current status, italicized, are as follows:

1. We have produced an automated routine to estimate seasonal air-sea CO₂ fluxes within 6 to 12-months of present utilizing remotely sensed SST, wind and other relevant products obtained from NESDIS and NASA. The seasonal estimates are posted on the web for comparison, validation, and initializing of models. *This is now a routine deliverable that is updated annually. Since the effort involves level-3 (fully quality controlled) satellite and assimilation data that is not available sooner than 6-months, the lag from present is 6-months to a year.*
2. The regional relationships of pCO_{2sw} and SST based on the Takahashi pCO_{2sw} climatology have been improved. The methodology has been validated by comparison with ongoing timeseries from moorings and Volunteer Observing Ships. *We are now using the Takahashi et al. (2009) climatology and are performing a thorough comparison of results with current data.*
3. The regional relationships of pCO_{2sw} and SST have been re-assessed using the pCO_{2sw} data obtained from the NOAA/OCO pCO₂ projects and affiliated efforts. *This has been done in part by applying the procedure to model output.*
4. Improved algorithms are developed utilizing other remotely sensed and high-density data in regions where the $\partial pCO_2 / \partial SST$ have poor predictive capabilities. *This is an ongoing effort and the focus of year-3. Our current analysis suggests that the method works extremely well in the subtropical gyres but has less fidelity at high latitudes and upwelling regions. We are investigating multi-annual relationships for these areas.*

Details of the work done in the first two years of this effort are listed in the results and accomplishment section below.

2.1. Method

Determination of monthly fluxes

For the quasi-operational product we are using the pCO_{2sw} climatology described in Takahashi et al. (2009) and empirical relationships between pCO₂ and SST that is described in detail in Park et al. (2006). In short, the flux of CO₂, F_{CO2} for every pixel and every month is calculated using the basic flux equation:

$$F_{CO2} = k K_0 (pCO_{2sw} - pCO_{2air})$$

Where k is the monthly mean gas transfer velocity, K_0 is the solubility of CO₂, pCO_{2sw} is the estimated pCO₂ in surface seawater using the $\partial pCO_2 / \partial SST$ algorithms. The monthly pCO_{2sw} for each latitude 4° × longitude 5° pixel for an individual year other than 2000 is estimated from the global ΔpCO_2 climatology from Takahashi et al. (2009), together with global records of SST anomalies compared with the climatology normalized to the year 2000 in the following manner:

$$pCO_{2swym} = [pCO_{2sw2000m} + (\partial pCO_{2sw} / \partial SST)_{2000m} \times \Delta SST_{ym-2000m}]$$

Where subscript "ym" is the year and month, and subscript "2000m" refers to the month in 2000.

The flux in turn is determined from:

$$F_{ym} = k_{ym} K_{0,ym} \{pCO_{2swym} - pCO_{2AIR2000m}\}$$

The solubility $K_{0,ym}$ is determined from monthly SST and climatological salinity using the solubility equations of Weiss (1974). We estimate k from the 2nd moment of the wind and the coefficients proposed in Sweeney et al. (2007):

$$k = 0.26 * 2^{nd} \text{ moment } (Sc/660)^{-0.5}$$

The 2nd moment is defined as $\sum U_{10}^2 / n$, where U_{10} is the wind speed at 10 m height obtained from the NCEP II reanalysis product. This procedure accounts for the variability in the wind. The 0.26 coefficient is different from that first proposed by Wanninkhof (1992) based on an improved assessment of the global ¹⁴C inventory used to constrain the global gas transfer velocity and a different wind product than used in the original work (see, Sweeney et al., 2007).

2.2. Results and Accomplishments

The results and accomplishments are presented in terms of the objectives outlined in the proposal.

- A. Produce an automated routine to quantify seasonal air-sea CO₂ fluxes from remotely sensed SST and wind: Following the procedures above and detailed in Park et al. (2006) a seasonal flux product is served from the AOML CO₂ website (<http://www.aoml.noaa.gov/ocd/gcc/movieoop.html>). Based on user feedback, we will provide anomaly maps, numerical tables and short descriptions of observed phenomena for the full 26-years we now have produced in year 3. An example of anomaly maps and descriptions can be found in Sabine et al. (2009) and is reproduced in Figure 1.
- B. The regional relationships of pCO_{2sw} and SST based on the Takahashi pCO_{2sw} climatology will be improved: We updated our procedure to incorporate the updated climatology presented in Takahashi et al. (2009). Furthermore we used a new wind speed product (NCEP II) and an updated gas exchange wind speed relationship (Wanninkhof et al., 2009). The unique algorithms between pCO_{2sw} and SST for El Niño and Non-El Niño periods for different time periods in the Eastern Equatorial Pacific (10°S-6°N, 165°E-280°E) are updated (Feely et al., 2006). Figure 2 shows the annual climatology as presented by Takahashi et al. (2009) along with the regional magnitude of interannual variability over the ocean. The average air-sea CO₂ flux over the past 25-years with this method is $-1.44 \pm 0.12 \text{ Pg C yr}^{-1}$. The results show a strong correlation with the ENSO cycle, which confirms a central hypothesis of our proposal that large-scale climate reorganizations have a key effect on interannual variability of air-sea CO₂ fluxes. Figure 3 shows the pixels where the

$\partial p\text{CO}_2/\partial \text{SST}$ relationships have changed from the previous climatology. Although the interannual variability globally has not changed appreciably between the two analyses, the regions of variability are appreciably different.

- C. Reassessment of regional relationships of $p\text{CO}_{2\text{sw}}$ and SST based on the Takahashi $p\text{CO}_{2\text{sw}}$ climatology. The central assumption of our approach that seasonal relationships between $p\text{CO}_{2\text{sw}}$ and SST are applicable to infer interannual variability in $p\text{CO}_{2\text{sw}}$ from interannual temperature anomalies is difficult to validate. Based on sparse time series reasonable agreement was found at the HOT and BATS time series and in the Equatorial Pacific (Park et al. 2006). In collaboration with Drs. S. Doney and I. Lima of WHOI we tested our approach using the output of the NCAR biogeochemistry model (Doney et al. 2009). The interannual variability of the model air-sea CO_2 fluxes can, in this manner, be directly compared with our empirical method. As shown in Figure 4 there is very good agreement both in magnitude and phasing of interannual variability in this comparison. The NCAR model shows an average net flux of $-1.55 \pm 0.17 \text{ Pg C yr}^{-1}$ while applying our approach using the model output $p\text{CO}_{2\text{sw}}$ yields $-1.49 \pm 0.13 \text{ Pg C yr}^{-1}$. The largest differences are observed in the Southern Ocean where our approach appears to underestimate variability.
- D. Improve algorithms utilizing other remotely sensed and high-density data in regions where the $\partial p\text{CO}_2/\partial \text{SST}$ have poor predictive capabilities. This will be a major focus of year-3 along with providing robust error estimates. From our analyses to date it is clear that high latitude regions will require an adapted approach. Figure 5 shows the correlation coefficients (r^2) of the relationships with correlations coefficients. In regions where $r^2 < 0.5$ it is assumed that there is no interannual change in $p\text{CO}_{2\text{sw}}$. The trends in $p\text{CO}_{2\text{sw}}$ are not well correlated with temperature in the boreal winter season and high latitudes. These are the areas of focus. Following Lueger et al. (2008) we are investigating if mixed layer depth provides an improved predictive capability in these regions.

3. REFERENCES

- Doney, S. C., I. Lima, R. A. Feely, D. M. Glover, K. Lindsay, N. Mahowal, J. K. Moore, and R. Wanninkhof, 2009: Mechanisms Governing Interannual Variability in the Upper Ocean Inorganic Carbon System and Air-Sea CO_2 Fluxes. *Deep-Sea Res II*.
- Feely, R. A., T. Takahashi, R. Wanninkhof, M. J. McPhaden, C. E. Cosca, and S. C. Sutherland, 2006: Decadal variability of the air-sea CO_2 fluxes in the equatorial Pacific ocean, *J. Geophys. Res.*, 111, doi:10.1029/2005JC003129.
- Gledhill, D. K., R. Wanninkhof, F. J. Millero, and M. Eakin, 2008: Ocean acidification of the greater Caribbean region 1996-2006. *J. Geophys. Res.*, 113, C10031, doi:10.1029/2007JC004629.
- Lueger, H., R. Wanninkhof, A. Olsen, J. Trinanes, T. Johannessen, D. Wallace, and A. Koertinger, 2008: The CO_2 air-sea flux in the North Atlantic estimated from satellite data and ARGO profiling float data, NOAA Technical Memorandum, OAR AOML-96, 28 pp.

Park, G.-H., K. Lee, R. Wanninkhof, and R. A. Feely, 2006: Empirical temperature-based estimates of variability in the oceanic uptake of CO₂ over the past 2 decades. *J. Geophys. Res.*, 111, doi:10.1029/2005JC003090.

Reynolds, R. W., T. M. Smith, C. Liu, D. B. Chelton, K. S. Casey, and M. G. Schlax, 2007: Daily high-resolution blended analyses for sea surface temperature. *J. Climate*, 20, 5473-5496.

Sabine, C., R. A. Feely, and R. Wanninkhof, 2009: The global ocean carbon cycle, in State of the Climate in 2008, edited by D. H. Levinson and J. H. Lawrimore, pp.. *Bull. Am. Meteorol. Soc.*, submitted.

Sweeney, C., E. Gloor, A. R. Jacobson, R. M. Key, G. McKinley, J. L. Sarmiento, and R. Wanninkhof, 2007: Constraining global air-sea gas exchange for CO₂ with recent bomb C-14 measurements. *Global Biogeochemical Cycles*, 21, doi:10.1029/2006GB002784.

Takahashi, T., S. C. Sutherland, R. Wanninkhof, C. Sweeney, R. A. Feely, D. W. Chipman, B. Hales, G. Friederich, F. Chavez, C. Sabine, A. Watson, D. C. E. Bakker, U. Schuster, N. Metzl, H. Y. Inoue, M. Ishii, T. Midorikawa, Y. Nojiri, A. Koertzing, T. Steinhoff, M. Hoppema, J. Olafsson, T. S. Arnarson, B. Tilbrook, T. Johannessen, A. Olsen, R. Bellerby, C. S. Wong, B. Delille, N. R. Bates, H. J. W. de Baar, 2009: Climatological Mean and Decadal Change in Surface Ocean pCO₂, and Net Sea-air CO₂ Flux over the Global Oceans. *Deep -Sea Res.*, in press.

Wanninkhof, R., W. E. Asher, D. T. Ho, C. S. Sweeney, and W. R. McGillis, 2009: Advances in Quantifying Air-Sea Gas Exchange and Environmental Forcing, *Annual Reviews Mar. Science*, 1, 213-244, 101146/annurev.marine.010908.163742.

Wanninkhof, R., 1992: Relationship between gas exchange and wind speed over the ocean. *J. Geophys. Res.*, 97, 7373-7381.

Weiss, R. F., 1974: Carbon dioxide in water and seawater: the solubility of a non-ideal gas, *Mar. Chem.*, 2, 203-215.

4. WEB LINKS

<http://www.aoml.noaa.gov/oce/gcc>

http://www.pmel.noaa.gov/CO2/uwpCO2/eq_pacific.html

5. FIGURES AND CAPTIONS

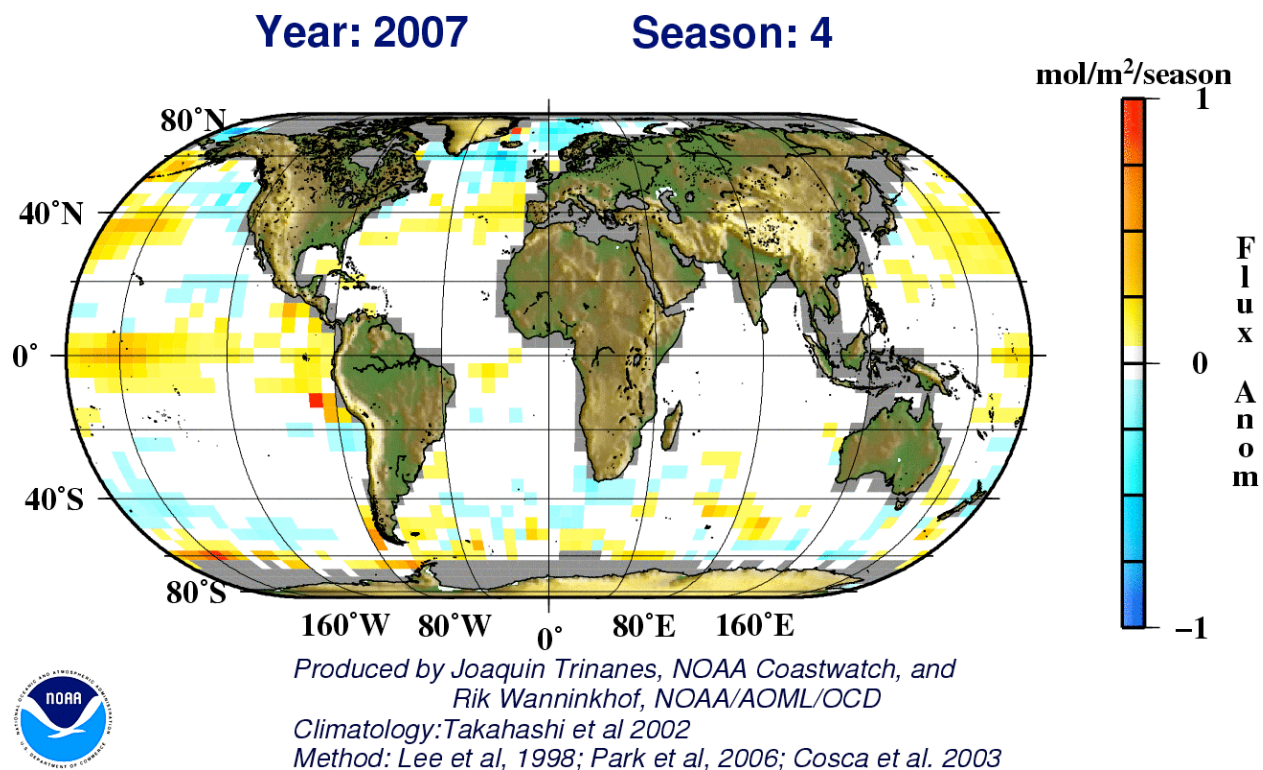


Figure 1. Map of the air-sea CO₂ flux anomaly for season 4 of 2007 (September-December) compared to the corresponding 25-year seasonal average (1982-2007). The figure clearly shows the large outgassing anomaly in the central and western Equatorial Pacific in response to the 2007/2008 La Nina event. Coastal pixels and those with ice cover are masked in gray.

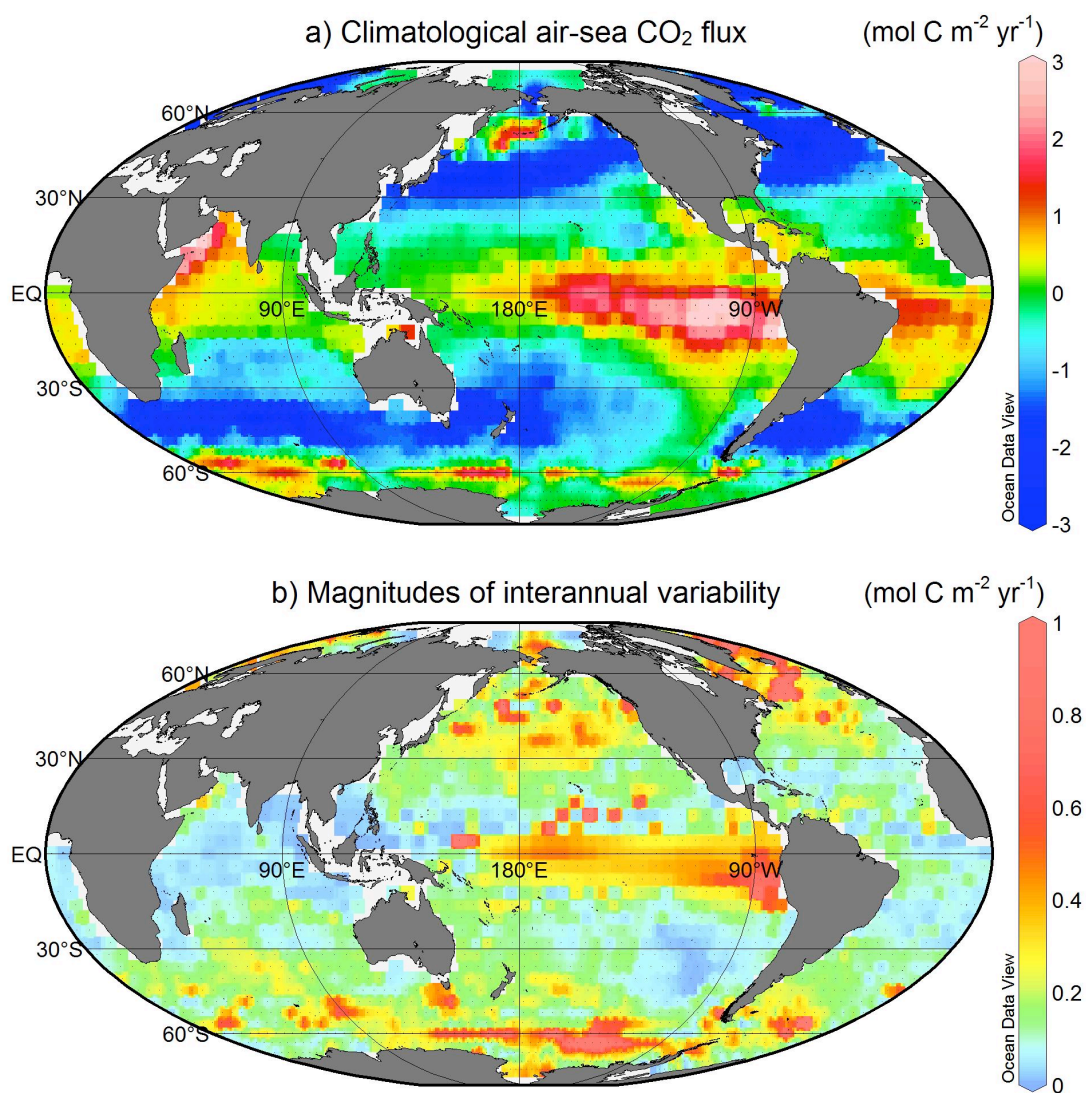


Figure 2. (a) Climatological air-sea CO₂ flux map from Takahashi et al. 2009 and magnitudes of interannual variability determined by our method. (plots provided by Dr. Geun-Ha Park, AOML/CIMAS)

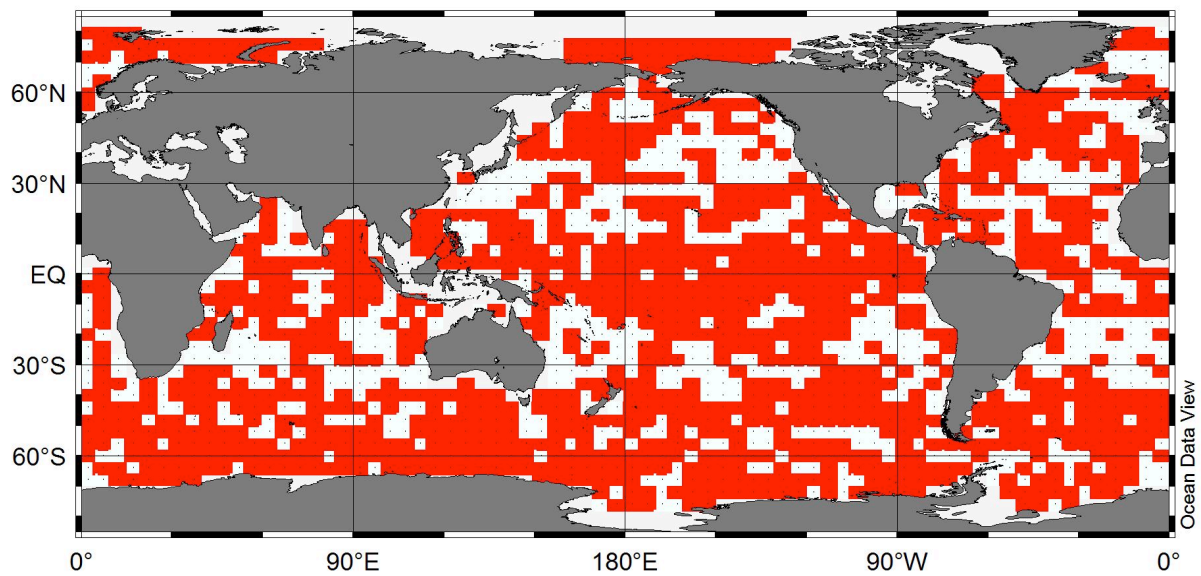


Figure 3. Map showing for which pixels the $\partial p\text{CO}_2/\partial \text{SST}$ relationships have changed between the Takahashi 1995 climatology and the Takahashi 2000 climatology which is now being used for our effort. The pixels colored red are those where the slope of the relationship changed signs in at least one of the seasons. (plots provided by Dr. Geun-Ha Park, AOML/CIMAS)

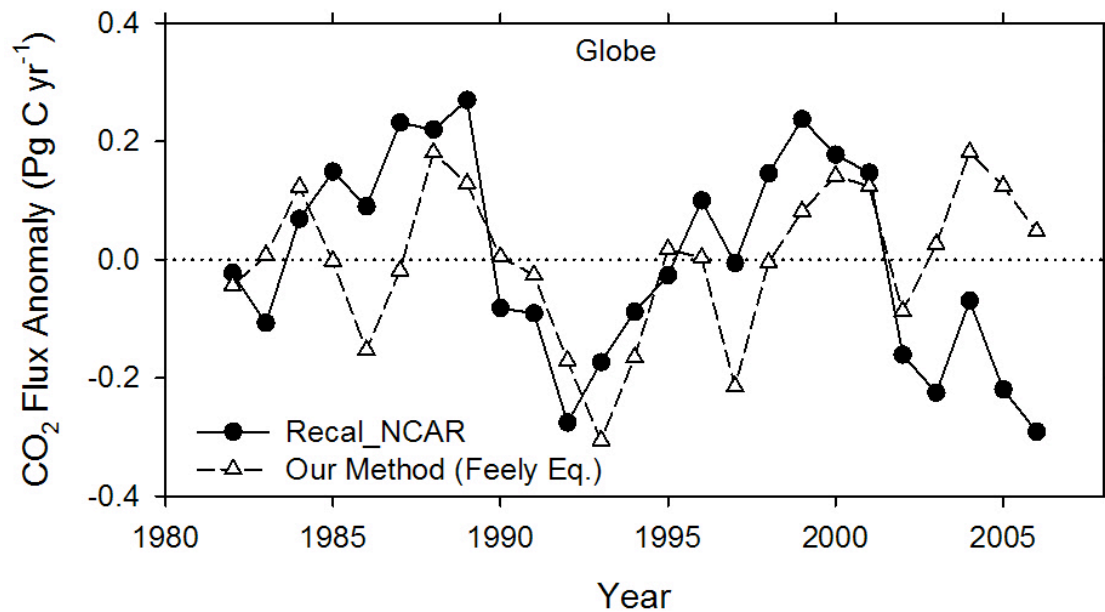


Figure 4. Comparison between the interannual variability of the NCAR model output (solid line with solid circles labelled "Recal_NCAR"), with our approach applied to the NCAR pCO_{2sw} output for year 2000 (dashed line with open triangles labelled "Our method (Feely Eq.)"). (plots provided by Dr. Geun Ha Park, AOML/CIMAS)

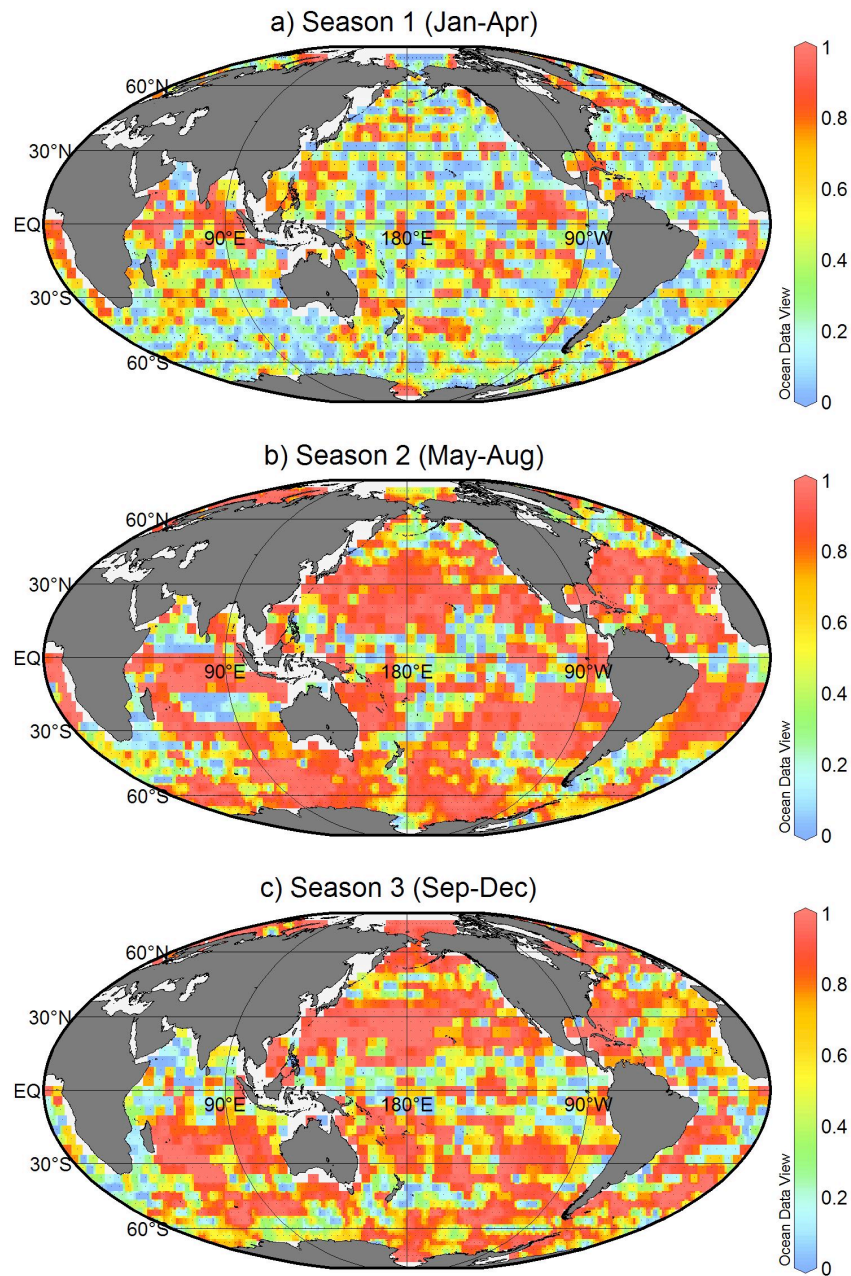


Figure 5. Seasonal maps providing the correlation coefficients of the $\partial p\text{CO}_2/\partial \text{SST}$ relationships derived from the Takahashi 2000 climatology (Takahashi et al. 2009). For pixels where $r^2 < 0.5$ it is assumed that there is no interannual variability in $p\text{CO}_{2\text{sw}}$. (plots provided by Dr. Geun-Ha Park, AOML/CIMAS)